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Dielectric Properties of Gelatin-Water System in a Megahertz Region

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Dielectric properties of gelatin-water system were measured in a frequency range of 1.3 to 100MHz. Both real and imaginary parts of dielectric constant had maxima at the gelatin concentration of 35%, which was ascribed to the saturation of bound water layer. The m-th power law was found to be applicable in a concentration range below 35% and a rather anomalous dielectric dispertion was observed at the concentration above 40%.

KEY WORDS: Dielectric properties/ Gelatin/ Bound water/ Protein solution/

INTRODUCTION

In aqueous protein solutions, bound water to the protein molecule plays a dominant role on dielectric properties of the system. In general, a dielectric dispersion spectrum exhibits three dispersions, that is, the orientational relaxation of protein molecule at low frequency, bound water relaxation at intermediate frequency between those for ice and water and free water relaxation.[1] Several models have been presented as to the states of bound water especially for globular proteins. Buchanan *et al.*[2] estimated the types of bound water as 'irrotationally' bound water to rotate in the high frequency field and 'not-irrotationally' bound water, depending on the degree of hydration and the axial ratio of protein molecule. According to the comment on bound water given by Celaschi and Mascarenhas,[3] it was classified into three groups; *i. e.* strongly bound water with very long relaxation times, first or subsequent water layers responsible for high frequency relaxation and liquid water nearest to the protein molecule. Harvey and Hockstra[4] claimed the existence of two layers of adsorbed water around protein molecule from dielectric measurement on moisten lysozyme, in which two distinct dispersions were observed at around 0.25GHz for the first layer and 10GHz for the second layer. Gelatin-water system was found to exhibit anomalous behavior in respect of dielectric dispersion. Fricke *et al.*[5,6] investigated dielectric properties of gelatin solutions and obtained the linear dependence of dielectric constant in log-log plots. They ascribed the origin of polarization to the orientation of 'interphasial' layer of water molecule in the disperse system. Masuzawa and Sterling[7] measured dielectric constants of various gel-water systems including gelatin. Although their experimental data were somewhat in conflict with those of Fricke and the present study in the concentration dependence of dielectric constant, they explained high dielectric constant of gelatin gel to be due to the larger amount of loosely bound water in gelatin than in agar, CMC and starch. Hanai[8] pointed

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out from the analysis of Fricke's data that anomalous dispersion of gelatin-water system might be assigned to the m-th power law or the wedge type dispersion which is sometimes observed in suspensions and some polymer systems.

In the present work, dielectric properties of gelatin-water system was investigated in detail at megahertz frequencies in order to clarify the bound water effect and check the applicability of the m-th power law.

EXPERIMENTAL

Gelatin powder from Difco Lab. was dried in an oven at 90°C for 24h to remove water before further treatment. The initial water content in the powder was estimated to be 12% from weight loss after drying. Dried powder was mixed with deionized water in a proper ratio for a certain concentration and a homogeneous solution was obtained by heating at 90°C for several hours. A concentration of gelatin in the solution was expressed in weight percent and the maximum concentration used in the present study was 60%. Impurity ions initially contained in gelatin solution were removed by means of electrodialysis so as to minimize the conductivity of the solution.

Dielectric measurements were carried out by using a Boonton RX-Meter Type 250-A in a frequency range of 1.3 to 100MHz and a TR-1C Ratio Arm Transformer Bridge in a frequency range below 2MHz. A sample cell for dielectric measurements was of Pyrex glass with rod-like shape platinum electrodes. Platinum black was deposited on the electrodes to suppress the electrode polarization effect which occurs in conductive aqueous samples in a low frequency region. The residual inductance in a megahertz region was estimated by using KCl solutions after a method proposed by Asami *et al.*[9] The measuring temperature was kept at 25°C by circulating water in a metal block around a sample cell.

RESULTS

The low frequency limit of conductivity κ_l was obtained by the extrapolation of a leveled part of a measured conductivity curve to 10Hz to avoid the electrode polarization effect which appears on a low frequency side and tends to decrease the conductivity. The imaginary part of dielectric constant ε'' was obtained from the equation of $\varepsilon''=(\kappa-\kappa_l)/\varepsilon_v\omega$, where κ is the measured conductivity, ω the circular frequency and ε_v the dielectric constant of vacuum. Thus, complex plane plots for gelatin-water system were made of the real part of dielectric constant ε' and ε'' in a frequency range of 1.3 to 100MHz, as shown in Fig. 1. As can be seen in this figure, the curves for gelatin concentrations below 35% fit in with a straight line (Fig. 1(a)), while this is not the case for those above 40%, that is, the plots deviate from a straight line below 10MHz for 40% and 45% and below 3MHz for 50% (Fig. 1(b)). For 60%, the plots can be roughly approximated by a straight line. In order to estimate the high frequency limit of dielectric constant ε_h, a straight line approximation was employed on a high frequency side for all the concentrations. The values of increment of dielectric constant $\Delta\varepsilon=\varepsilon'-\varepsilon_h$ were thus obtained. In Fig. 2, log $\Delta\varepsilon'$ and log ε'' were plotted against log f. Straight

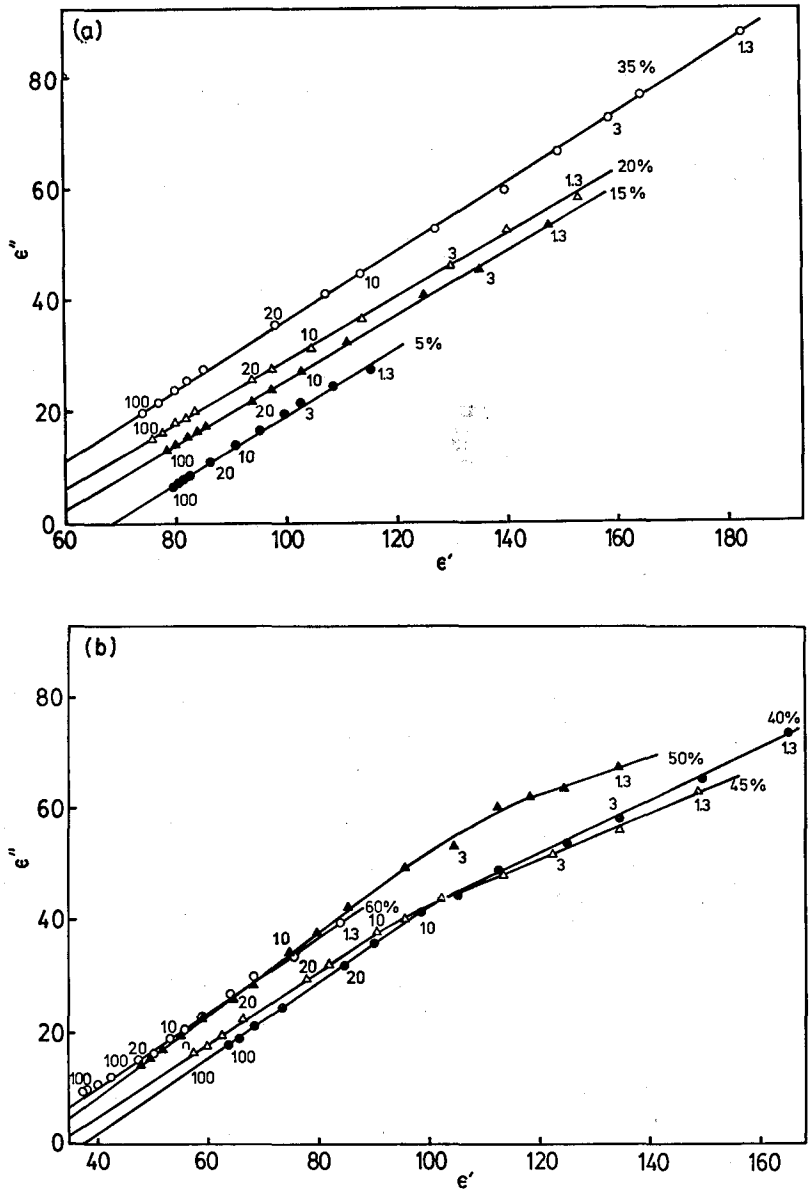

Fig. 1. Complex plots for gelatin-water system: (a) below 35% (b) above 40%. Numbers in the figure represent frequencies in megahertz.

lines were obtained in log $\Delta\varepsilon'$—log f plots for all the concentrations and in log ε''—log f plots for the concentrations below 35% (Fig. 2(a), (b) and (c)). The log ε''—log f plots were curved below 10MHz for 40% and 45% and below 3MHz for 50% (Fig. 2 (d)). For 60%, both the log $\Delta\varepsilon'$—log f and the log ε''—log f plots deviate from a straight line on a high frequency side. These trends are consistent with those of complex plane plots in Fig. 1.

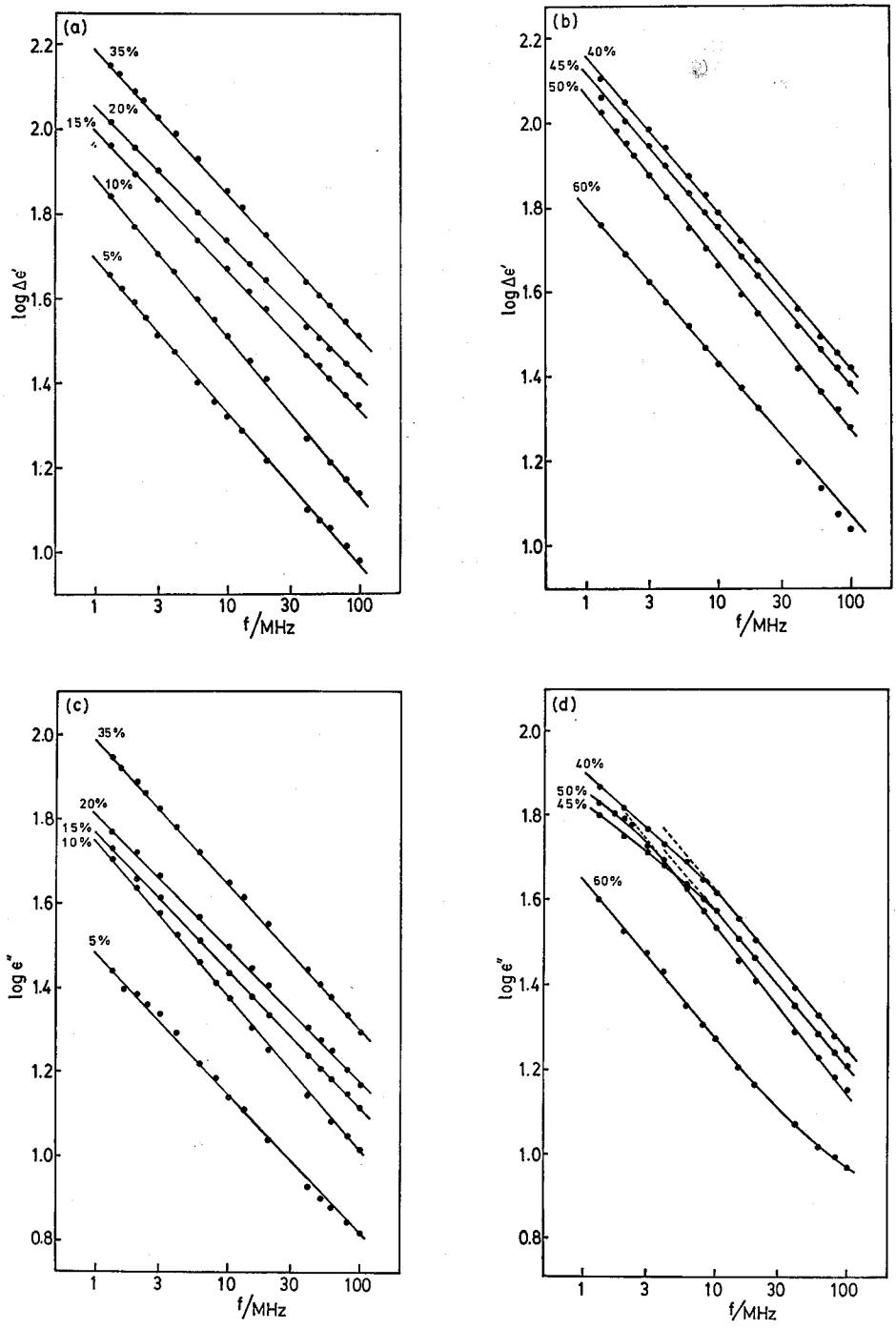

Fig. 2. Frequency depenedenc of $\Delta\varepsilon'$ and ε'': (a) and (b) log $\Delta\varepsilon'$ *vs.* log f plots (c) and (d) log ε'' *vs.* log f plots.
Broken lines are straight lines extrapolated from linear parts on a high frequncy side.

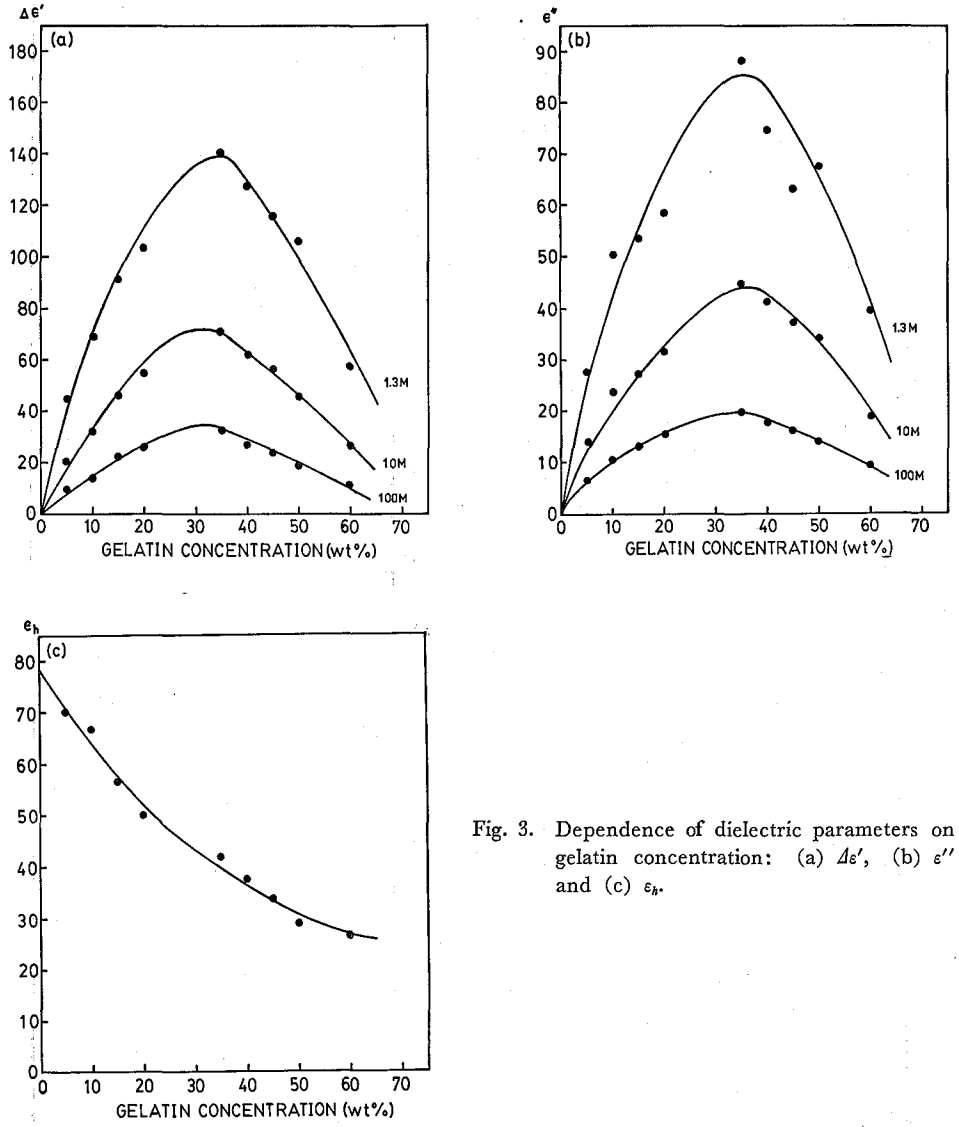

Fig. 3. Dependence of dielectric parameters on gelatin concentration: (a) $\Delta\varepsilon'$, (b) ε'' and (c) ε_h.

In Fig. 3 is shown the concentration dependence of $\Delta\varepsilon'$ and ε'' at frequencies of 1, 3, 10 and 100MHz and ε_h. It is noted that $\Delta\varepsilon'$ and ε'' curves have maxima at around 35%, while ε_h decreases continuously with increasing gelatin concentration.

Preliminary experiments showed that dielectric properties were not affected by electrodialysis even though the conductivities were decreased.

DISCUSSION

The presence of maxima in $\Delta\varepsilon'$ and ε'' *vs.* gelatin concentration curves at around

35% in Fig. 3 suggests that the amount of bound water is related to the magnitude of dielectric constant. Namely, increments of both $\Delta\varepsilon'$ and ε'' with increasing gelatin concentration below 35% correspond to increment of the amount of bound water. At the concentration of 35%, the amount of bound water is saturated in the sense of dielectric polarization so that the maximum $\Delta\varepsilon'$ and ε'' appear. Subsequently the shortage of bound water for the total gelatin molecules causes the decrease of $\Delta\varepsilon'$ and ε'' with increasing gelatin concentration above 35%. These results are consistent with those of Fricke,[6] who obtained maximum $\Delta\varepsilon'$ at the concentration of 45% at 16kHz. Assuming that gelatin molecule is of a chain structure with molecular weight of ~100, 000 and consists of 1280 amino acid residues,[10] the number of water molecule bound to one amino acid residue is estimated to be approximately ten at the concentration of 35%. This value corresponds to 1. 86 g water per g gelatin, which is far more than 0. 40 g water per g gelatin for the total bound water estimated by Buchanan[2] on the assumption that bound water was attached to a protein molecule directly. It may be suggested that bound water which affects dielectric polarization forms a multilayer structure. The concept of bound water is also supported by the dependence of ε_h on gelatin concentration in Fig. 3(c). The rapid decrease of ε_h with increasing gelatin concentration corresponds to a decrease of the amount of free water by adding gelatin in the solutions. Since water molecules attach to gelatin molecule rather loosely as observed in NMR study by Sterling and Masuzawa,[11] ε_h retains somewhat large values at higher concentrations than 35% at which bound water is saturated.

The complex plane plots give straight lines for concentrations below 35% in Fig. 1(a), which is characteristic of the m-th power law. Moreover, it is confirmed by the fact that log $\Delta\varepsilon'$ and log ε'' plots give straight lines against log f as is seen in Fig. 2(a) and (c). According to the formulation for the m-th power law given in the paper by Koizumi and Hanai[12], the value of m is obtained from the slope of complex plane plots by the equation of slope=tan $m\pi/2$ and m is equal to both slopes of log $\Delta\varepsilon'$ and log ε'' *vs.* log f plots (slope ($\Delta\varepsilon'$) and slope (ε''), respectively). In Table I, m, slope ($\Delta\varepsilon'$) and

Table I Parameters of the m-th power law obtained from $\varepsilon'-\varepsilon''$(m), log $\Delta\varepsilon'$—log f (slope ($\Delta\varepsilon'$)) and log ε''—log f (slope (ε'')) relations.

concentration	m	slope ($\Delta\varepsilon'$)	slope (ε'')
5%	0. 375	0. 371	0. 348
10%	0. 401	0. 378	0. 378
15%	0. 338	0. 330	0. 325
20%	0. 334	0. 324	0. 320
35%	0. 353	0. 341	0. 339
40%[a]	0. 377	0. 374	0. 379
45%[a]	0. 373	0. 371	0. 368
50%[a]	0. 404	0. 394	0. 397
60%[b]	0. 387	0. 366	0. 367

a) obtained from the data on a high frequency side.
b) obtained by a straight line approximation.

slope(ε'') are listed and these three values are equal within experimental error supporting the m-th power law. The value of m is independent of gelatin concentration and lies in a range of 0.33 to 0.40. Although the exact mechanism of the m-th power law is still unclear, Koizumi *et al.*[13] attributed the origin of the m-th power law to the space charge polarization due to ionic impurities in the study of VDF-TEF copolymers. The same trend was also observed in dielectric measurements of PVDF.[14] This mechanism might be ruled out in the present system because the addition of KCl to gelatin solution was found to have no effect on dielectric polarization. On the other hand, adsorbed water seemed to have an effect on the m-th power law suggested from the study of solid polyethylene glycols[12] and titanium oxide particles in paraffin.[15] This might be applicable to gelatin-water system.

In a concentration range above 35% at which dielectric constants have maximum values, both the complex plane plots in Fig. 1(b) and the $\log \varepsilon'' - \log f$ plots in Fig. 2(d) definitely deviate from those expected from the m-th power law. Therefore, other types of dispersion were examined so as to fit the experimental curves with calculated ones. As a result, only the Cole-Cole type dispersion[16] was found to give fair agreement between experimental and calculated curves for 40% and 45% by using α of 0.58 and 0.56, respectively. But in the case of 50% and 60%, this attempt turned out unsuccessful. Although full explanation for this anomalous behavior can not be given in the present study, it is suggeted that deficient bound water layer in concentrated gelatin solutions might change the state of dielectric polarization.

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